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16. ABSTRACT The report describes an analysis of arsenic as the oxo anion. The procedure involves oxidation of the arsenic to arsenate in an aqueous solution and injection onto an anion separartor column. Comparison is made with a standard wet chemical procedure, and data is presented on reproducibility. Ther is also a discussion of the applicability of this method to the determination of other oxo anions.

In the past few years the technique of ion chromatography, as developed by Small,Stevens, and Baumann, has proven useful in a wide range of analytical applications. In particular, the determination of such species as Cl(-), F(-), NO2(-), NO3(-), SO 3(=), and SO4(=) by anion separation column has rendered many long and complicated wet chemical procedures obsolete. In this technique the anions of interest are separated on an analytical column containing fine anion exchange particles agglomerated on surface sulfonated styrene divinylbenzene(SSS/DVB) resin. They are then passed through a strong acid stripper column from which they are eluted in a background of de-ionized water. The concentration is measured by a conductivity cell in conjunction with a strip chart recorder.

17. KEY WORDS AND DOCUMENT ANALYSIS

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Analyzing	Stationary Sources	14B
Arsenic	Ion Chromatography	7B
Arsenates		7D
Oxidation		7B

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DETERMINATION OF ARSENIC AS THE OXIDATE BY ION CHROMATOGRAPHY

KEY WORDS · arsenic, ion chromatography, anion exchange, arsenate

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ABSTRACT

An ion chromatographic procedure is described for the analysis of arsenic as the oxo anion. The procedure involves oxidation of the arsenic to arsenate in an aqueous solution and injection onto an anion separator column. Comparison is made with a standard wet chemical procedure, and data is presented on reproducibility. In addition, there is a brief discussion of the applicability of this method to the determination of other oxo anions.

In the past few years the technique of ion chromatography (I.C.) as developed by Small, Stevens, and Baumann [1] has proven itself useful in a wide range of analytical applications. In particular, the determination of such species as Cl^-, F^-, NO_2^-, NO_3^-, $SO_3^=$, and $SO_4^=$ by anion separation column has rendered many long and complicated wet chemical procedures obsolete. In this technique the anions of interest are separated on an analytical column containing fine anion exchange particles agglomerated on surface sulfonated styrene divinylbenzene (SSS/DVB) resin. They are then passed through a strong acid (H^+) stripper column from which they are eluted in a background of de-ionized water. Measurement of the concentration is accomplished by means of a conductivity cell used in conjunction with a strip chart recorder.

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I.C. readily lends itself to the analysis of arsenic. Using this procedure, arsenic dissolved in a liquid medium is first converted to arsenate and then injected neat onto an anion separator column, using a solution of sodium carbonate and sodium bicarbonate as the eluent. After approximately 17 minutes, depending on the column and conditions used, an arsenate peak will elute, and the concentration can be determined by comparison with a standard calibration curve. Because I.C. is a separation technique, the interferences experienced with other types of arsenic determinations are not normally a problem. When encountered, however, they can usually be dealt with by diluting the eluent. This enhances the affinity of the anion for the exchange resin and increases retention times, resulting in better resolution of the peaks. Conversion of arsenic to arsenate poses no special problems. Once in solution, most arsenic compounds can readily be oxidized to arsenate. For example, arsenite can be converted to arsenate simply by rendering the solution alkaline and adding a few drops of 0.1 M calcium hypochlorite solution. [2]

EXPERIMENTAL

APPARATUS

Separator Column. One 3x500 mm glass column packed with SSS/DVB and fine mesh anion exchange resin.

Stripping Column. One 6x250 mm glass column packed with cation exchange resin in the hydrogen (H^+) form.

Eluent. A solution of distilled deionized water containing 0.25 grams/liter sodium bicarbonate and 0.25 grams/liter sodium carbonate. The eluent flow rate was 1.5 ml/min.

A block diagram of the ion chromatographic system used appears in Figure 1.

REAGENTS AND PROCEDURE

A series of synthetic samples containing 4-20 µg/ml arsenic pentoxide (2.6-12.8 µg/ml arsenic) was made up in distilled deionized water using reagent grade materials. The samples were then divided into two equal portions. One portion was analyzed colorimetrically using the silver diethyldithiocarbamate method. [3] The second portion of the sample was injected neat onto an anion separator column,

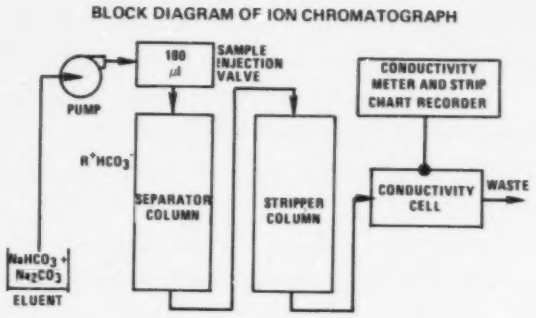

Figure 1. Block diagram of ion chromatograph.

using a 100 µl injection loop. The concentration was then determined by comparison with a standard calibration curve.

Figure 2 shows a typical arsenic chromatogram.

RESULTS AND CONCLUSION

Excellent agreement was observed between the known concentrations in the samples and the concentrations as determined by the I.C. method. Good agreement was also noted between the I.C. and the silver diethyldithiocarbamate results. However, it was evident that the I.C. method generally provided results with a

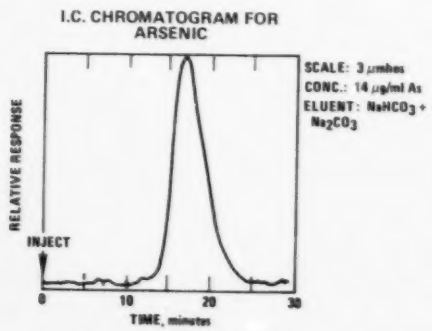

Figure 2. I.C. chromatogram for arsenic.

closer correspondence to the known arsenic values. Table 1 presents the data from these tests.

Table 2 presents the standard deviations for the I.C. analysis of four known concentrations of arsenic. Each data point represents at least eight replicate analyses. As can be seen, the results fall well within acceptable limits of tolerance.

The authors have used this analytical procedure on actual environmental samples. Figure 3 shows an ion chromatogram of leachate from a 10 gram sample of particulate matter acquired at a copper smelter. In addition to arsenate, the anions fluoride, chloride, nitrate, and sulfate and the metal ions lead, cadmium, copper, antimony, mercury and nickel were found in this sample in relatively large quantities. Neither the anions nor the metal ions had any effect on the analysis for arsenic. The I.C. result of 81.9 mg arsenic per gram of particulate matter corresponded favorably with a silver reagent method determination of 78.6 mg per gram.

Table 1

Comparison of Arsenic Analytical Methods

Actual Concentration	Ion Chromatograph Determination	Silver Reagent Determination
2.6	2.7	2.5
5.2	5.2	5.2
7.8	7.8	8.1
10.4	10.4	10.6
12.8	12.9	12.5

All results are given in μg/ml.

Table 2

Reproducibility of I.C. Analysis of Arsenic

Concentration (μg/ml)	Area ($\bar{X}$)	Standard Deviation (area units)
5.2	1234.4	19.58
7.8	1895.2	20.24
10.4	2595.2	11.74
12.8	3155.5	18.35

$\bar{X}$ = arithmetic mean

CHROMATOGRAM OF LEACHATE FROM COPPER SMELTER

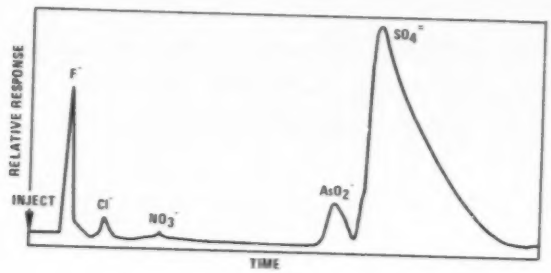

Figure 3. Chromatogram of leachate from copper smelter.

The I.C. method described above can also be applied to the analysis of other oxo anions. In fact, the technique of preliminary oxidation followed by I.C. analysis would seem to be generally applicable to Group VA, VIA and VIB elements with the greater ease of oxidation being found in the earlier members of each group. The I.C. determination of chromium as CrO_4 is already a routine procedure in many laboratories, and the authors have successfully used I.C. in the determination of vanadium as V_2O_5 and selenium as SeO_3. Promising results have also been achieved in the qualitative analysis of artificial samples containing the oxo anions of antimony. However, the general insolubility of the oxides of this metal in any media suitable for I.C. injection makes this an uncertain procedure for quantitative analysis.

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